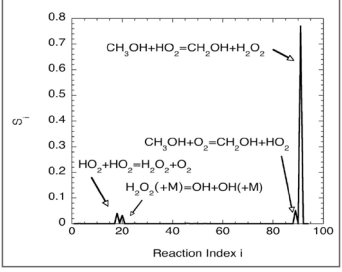
Theoretical Validation of Chemical-kinetic Reaction Mechanisms

Chemical kinetics modeling is an important aspect of designing efficient renewable fuels.

The Challenge

Modeling the combustion chemistry of even a simple fuel such as heptane requires information on hundreds of chemical species and thousands of chemical reactions. Combustion modelers typically assemble the best available data on chemical species and reactions, but this information is often incomplete or has large uncertainties.

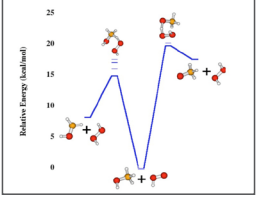
Important chemical reactions are identified with global sensitivity analysis.



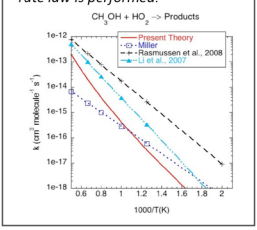
The Solution

To address this gap in the development of predictive models, Argonne chemists have initiated a program for the validation of chemical-kinetic mechanisms based on first-principle theoretical methods. This project is part of a larger effort from Argonne's Chemical Dynamics group to implement DACE (Design and Analysis of Computer Experiments) methodology into the study of complex chemical kinetics and related phenomena. Through this program, Argonne is strengthening its capabilities to solve chemical-kinetic problems important to combustion science by creating a feedback loop to link the experimental, theoretical and modeling components of the group's efforts.

State-of-the art quantum chemistry techniques are used to describe the energetics of the key reaction.



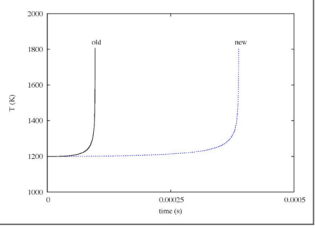
First-principle calculation of the rate law is performed.



The Results

A first study, in collaboration with researchers from the University of Colorado and the University of Leeds, is focused on determining the sensitivity of predicted ignition times of methanol/air mixtures as modeled by a chemical-kinetic mechanism (see figures at right). Further optimizations of the mechanism can be accomplished by studying other physical or chemical characteristics that it predicts, such as the behavior of steady flames or the ignition characteristics of formaldehyde. By improving the information available with chemical-kinetic mechanisms, Argonne researchers hope to develop a more effective predictive model for engine and fuel design.

With an improved mechanism, the new rate law leads to much longer times for ignition, which is indicated by the sharp rise in temperature.



***"This work demonstrates the feasibility of a rational means for the theoretical validation of complex chemical-kinetic mechanisms,"* said Michael J. Davis, senior chemist, Argonne National Laboratory.**